

PATENT ABSTRACTS OF JAPAN

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(54) RESIN COMPOSITION FOR TONER, AND TONER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a resin composition for toner and a toner maintaining good offset resistance, low temperature fixing property and storage property and causing no fog due to production of fine powder in a developing machine.

SOLUTION: The resin composition for toner essentially comprises a polyester block copolymer having 3×10^3 to 5×10^4 weight average mol.wt. and containing polyester blocks by condensation of aliphatic diols and dicarboxylic acids and polyester blocks by condensation of alicyclic diols and dicarboxylic acids.

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CLAIMS

[Claim(s)]

[Claim 1] Weight average molecular weight 3×10^3 to 5×10^4 which contains in a molecule an aliphatic diol, the polyester block which comes to condense dicarboxylic acids, and an alicyclic group diol and the polyester block which comes to condense dicarboxylic acids Resin constituent for toners characterized by making a polyester block copolymer into a principal component.

[Claim 2] The resin constituent for toners according to claim 1 characterized by the bird clapper from the polyester block copolymer containing 10-55 mol % of polyester block components which comes to condense an aliphatic diol and dicarboxylic acids, and an alicyclic group diol and 90-45 mol % of polyester block components which comes to condense dicarboxylic acids.

[Claim 3] The resin constituent for toners according to claim 1 or 2 which contains phthalic anhydride as the above-mentioned dicarboxylic acids, and is characterized by the bird clapper.

[Claim 4] The resin constituent for toners according to claim 1 to 3 characterized by for a glass transition point being 50 degrees C or more, and softening temperature being 130 degrees C or less.

[Claim 5] The resin constituent for toners which blends with the resin constituent for toners according to claim 1 to 4 the bridge formation polyester polymer which does not contain the bisphenol A derivative as a diol component, and is characterized by the bird clapper.

[Claim 6] The toner which contains the resin constituent for toners according to claim 1 to 5, and is characterized by the bird clapper.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[The technical field to which invention belongs] this invention relates to the resin constituent for toners and toner which are used for the so-called dry-developing method of the methods which develop an electrostatic-charge image in detail about the resin constituent for toners and toner which are used for electrophotography, a copying machine, a printer, etc.

[0001]

[Description of the Prior Art] As a method which develops an electrostatic-charge image in electrophotography etc., the dry-developing method is used abundantly. In a dry-developing method, usually, a toner is charged by friction with iron powder or a glass bead called carrier, and this adheres to the electrostatic latent image on a photo conductor with electric attraction, next, it is imprinted on a form, and a hot calender roll etc. is fixed to it, and it serves as a permanent visible image.

[0002] The heating roller method performed by making it pass, making the toner picture of an established sheet ***** on the front face of the heating roller which formed the front face with the material which has a mold-release characteristic to a toner as the method of fixing is used abundantly. In this heating roller method, in order to raise economical efficiency, such as power consumption, and in order to gather copy speed, the toner which can be established at low temperature is called for.

[0003] However, when it is going to improve the above-mentioned low-temperature fixing nature, a part of toner adheres to a heat fixing roller front face, and there is a problem that will become or shelf life will fall that the offset phenomenon that it re-prints on paper tends to happen.

[0004] Many attempts in which low-temperature fixing nature, offset-proof nature, and shelf life are made to improve occur to these problems by using the bisphenol A derivatives, such as the bisphenol A alkylene oxide addition product, as a diol component of polyester resin. However, there arises misgiving of the internal secretion disturbance matter in bisphenol A, and it is beginning to be thought in recent years that it is not desirable to use it as a raw material of the toner which is the fine particles which are easy to disperse. In addition, use of bisphenol A derivative content polyester resin is presenting the problem in degradation of the color of a toner and a pigment, or the lightfastness after fixing.

[0005] Priority is given over the bisphenol A derivative which has such a problem, and the method using an alicycle group diol is proposed. For example, the toner for electrophotography which made the polyester resin obtained by the condensation polymerization of the multiple-valued carboxylic acids it is incomparable to JP,4-337741,A from the diol which consists of an alicycle group diol and an aliphatic diol, an aromatic dicarboxylic acid, and the multiple-valued carboxylic acid more than trivalent the main constituent of a binding material resin is indicated.

[0006] However, although offset-proof nature may improve when the toner indicated by the above-mentioned official report constructs a bridge by the multiple-valued carboxylic acid, low-temperature fixing nature is not enough.

[0007] Moreover, the attempt which offset-proof nature and low-temperature fixing nature tend to be made to balance, and is going to cope with the above-mentioned problem also occurs. There is the method of blending the low-molecular-weight polyester resin for improving for

example, low-temperature fixing nature and the amount polyester resin of macromolecules for improving offset-proof nature as these attempts. However, the diol component which becomes low-molecular-weight polyester resin from an alicycle group diol and an aliphatic diol using the above-mentioned method, The polyester resin obtained by carrying out condensation polymerization of the dicarboxylic-acid component at random Balance with many properties relevant to low-temperature fixing nature, shelf life, or resin intensity is difficult, if you are going to make it improve low-temperature fixing nature, toner shelf life will fall, or resin intensity will fall, generating of fines will become remarkable within a developing machine, and the problem of the another kind of becoming easy to come out of fogging will be caused.

[0008]

[Problem(s) to be Solved by the Invention] this invention aims at offering the resin constituent for toners and toner which it is going to improve [toner] the above-mentioned fault, and make both offset-proof nature low-temperature fixing nature and shelf life hold good, and do not generate fogging by generating of fines within a developing machine.

[0009]

[Means for Solving the Problem] The resin constituent for toners of invention according to claim 1 is the weight average molecular weight 3×10^3 to 5×10^4 which contains in a molecule an aliphatic diol, the polyester block which comes to condense dicarboxylic acids, and an alicycle group diol and the polyester block which comes to condense dicarboxylic acids. Let a polyester block copolymer be a principal component.

[0010] The resin constituent for toners of invention according to claim 2 consists of a polyester block copolymer containing 10-55 mol % of polyester block components which comes to condense an aliphatic diol and dicarboxylic acids in the resin constituent for toners of invention according to claim 1, and an alicycle group diol and 90-45 mol % of polyester block components which comes to condense dicarboxylic acids.

[0011] The resin constituent for toners of invention according to claim 3 comes to contain phthalic anhydride as the above-mentioned dicarboxylic acid in the resin constituent for toners of invention according to claim 1 or 2.

[0012] In the resin constituent for toners of invention according to claim 1 to 3, a glass transition point is 50 degrees C or more, and the softening temperature of the resin constituent for toners of invention according to claim 4 is 120 degrees C or less.

[0013] The resin constituent for toners of invention according to claim 5 comes to blend with the resin constituent for toners of invention according to claim 1 to 4 the bridge formation polyester polymer which does not contain the bisphenol A derivative as a diol component.

[0014] The toner of invention according to claim 6 comes to contain the resin constituent for toners according to claim 1 to 5.

[0015] Although especially the aliphatic diol used by this invention is not limited, ethylene glycol, diethylene-glycol, triethylene-glycol, 1, 2-propylene-glycol, 1, 3-propylene-glycol, 1, 4-butanediol, 2, and 2-dimethyl propane -1, 3-diol, a polyethylene glycol, a polypropylene glycol, a polytetramethylene glycol, etc. are mentioned, for example.

[0016] Although especially the above-mentioned alicycle group diol is not limited, the alkylene oxide addition product of 1, 4-cyclohexane diol, 1, 4-cyclohexane dimethanol, hydrogenation bisphenol A, and hydrogenation bisphenol A etc. is mentioned, for example.

[0017] Although the above-mentioned dicarboxylic acids are a carboxylic acid, its divalent acid anhydride, or its divalent low-grade alkyl ester and it is not limited especially, a phthalic acid, a terephthalic acid, an isophthalic acid, a succinic acid, an adipic acid, a sebacic acid, an azelaic acid, an octyl succinic acid, a cyclohexane dicarboxylic acid, a fumaric acid, a maleic acid, itaconic acids and these acid anhydrides, low-grade alkyl ester, etc. are mentioned, for example. Especially, phthalic anhydride is suitably used in that the ease of progressing of an esterification reaction and the fall of a glass transition point (T_{mg}) can be suppressed.

[0018] Especially the method of preparation of the aliphatic diol used by this invention, the polyester block (it is hereafter called the polyester block A for short) which comes to condense a dicarboxylic acid, and the polyester block (it is hereafter called the polyester block B for short) which comes to condense an alicycle group diol and a dicarboxylic acid is not limited, and can be

obtained by the polyester condensation polymerization reaction according to a conventional method. Moreover, the polyester block copolymer containing the polyester block A and the polyester block B can acquire the above-mentioned polyester block A and the polyester block B according to a conventional method by the dehydration condensation polymerization reaction and the ** diol condensation polymerization reaction. In addition, the manufacture method of the above-mentioned polyester block copolymer used by this invention is not limited only to the above-mentioned manufacture method.

[0019] The weight average molecular weight of the above-mentioned polyester block copolymer was measured by the gel permeation chromatography (GPC). It used "KF-800P" (1) by Showa Denko K.K., "KF-806M" (2), and "KF-802.5" (1), GPC's having connected "HTR-C" by the Nihon Millipore Limited, Inc. as equipment, and having connected in series as a column. Measurement conditions were set to temperature [of 40 degrees C], 0.2 % of the weight THF solution [of sample concentration] (what passed 0.45-micrometer filter), and injection-rate 100microl, and standard polystyrene was used for them as a proofreading sample.

[0020] The weight average molecular weight of the above-mentioned polyester block copolymer is 3x103. In the following, resin intensity becomes small, and the toner obtained generates fines within a developing machine, and it becomes easy to cause fogging, and is 5x104. Since the fixing nature of a toner may fall when it exceeds, it is 3x103 to 5x104. It is limited to the range.

[0021] As for the content ratio of the polyester block A and the polyester block B in the above-mentioned polyester block copolymer, it is desirable that it is polyester block B 90-45-mol % to polyester block A 10-55-mol %. When it separates from the above-mentioned range, there is a possibility of the balance of low-temperature fixing nature, shelf life, and resin intensity becoming bad, and leading to the trouble mentioned above.

[0022] Since shelf life may fall when it becomes not much low, as for the glass transition temperature (Tmg) of the resin constituent for toners of this invention, it is desirable that it is more than Tg50 degree C. In addition, Above Tmg is JIS. K It is measured based on 7121 and the midpoint glass transition temperature indicated by this specification (9.3 "how to ask for a glass transition temperature") is meant.

[0023] Moreover, since fixing nature will fall if it becomes not much high, as for the softening temperature of the resin constituent for toners of this invention, it is desirable that it is 130 degrees C or less. In addition, the above-mentioned softening temperature is measured according to the measurement conditions of the flow softening temperature shown in Table 1 using a quantity-ized formula flow tester (the Shimadzu Corp. make, "CFT-500 type"), and means the temperature of the point T on the flow curve equivalent to h/2 of the flow charts for analysis shown in drawing 1 (flow softening temperature).

[0024]

[Table 1]

項 目	条 件
測 定 機 器	高化式フローテスター (島津製作所CFT-500型)
測 定 試 料	1.00 g (目開き 1.18mmのJIS標準篩通過物)
荷 重	20 Kg/cm ²
オ リ フ ィ ス	1 mmφ × 1 mm
予 備 温 度	40℃ (1-用樹脂組成物の場合80℃)
予 備 時 間	5 分
チャート速度	20 mm/min
プランジャー	1.0 cm ²
昇 温 速 度	6±0.5 °C/min

[0025] The above-mentioned softening temperature is 120 degrees C still more preferably, if it

changes with kinds of stain pigment used as a colorant mentioned later etc. and is in the resin constituent for full color toners, and if it is in the resin constituent for monochrome color toners, it is more desirable than the resin constituent for full color toners that it is 130 degrees C or less of elevated-temperature approach a little.

[0026] It is desirable for the bridge formation polyester polymer (for it to only be hereafter called a bridge formation polyester polymer for short) which does not contain the bisphenol A derivative as a diol component to blend with the above-mentioned polyester block copolymer, and to prepare the resin constituent for toners. Of course, although it may be necessary to be combination of a bridge formation polyester polymer, offset-proof nature is notably improvable [to the resin constituent for monochrome toners] depending on the kind of stain pigment which is used as a coloring agent and which is mentioned later, especially with combination of the above-mentioned bridge formation polyester polymer.

[0027] After eliminating the bisphenol A derivative with the misgiving of the internal secretion disturbance matter, and carrying out condensation polymerization of the carboxylic acids more than trivalent and/or the alcohol more than trivalent, and dicarboxylic acids and a diol by the conventional method, for example, carrying out condensation polymerization of dicarboxylic acids and the diol by the conventional method, the above-mentioned bridge formation polyester polymer makes cross linking agents, such as a diisocyanate compound and an epoxy compound, react, and is obtained.

[0028] Since the improvement effect of offset-proof nature will not appear the flow softening temperature of the above-mentioned bridge formation polyester polymer if fixing nature will fall if not much high, and it is not much low, it is 120-200 degrees C preferably. Moreover, since shelf life will fall if not much low, the glass transition point (Tmg) of the above-mentioned bridge formation polyester polymer is 50 degrees C or more preferably.

[0029] The loadings ratio of a bridge formation polyester polymer to the above-mentioned polyester block copolymer Since the improvement effect of offset-proof nature will not appear if not much low [in the case of the resin constituent for monochrome toners, if the loadings ratio of a bridge formation polyester polymer is not much high, fixing nature will fall, and] Although it is desirable that it is 80 - 10 % of the weight of bridge formation polyester polymers, and the improvement effect of offset-proof nature is accepted by content of the bridge formation polyester polymer of an amount a little to 20 - 90 % of the weight of polyester block copolymers when it is a resin constituent for full color toners [if blended not much with a large quantity, since fixing nature will be reduced on the contrary, it is desirable that it is 0 - 20 % of the weight of bridge formation polyester polymers to 100 - 80 % of the weight of polyester block copolymers.

[0030] Resins other than the bridge formation polyester polymer to polyester block copolymers, such as vinyl system copolymerization resins, such as styrene-acrylic resin, an epoxy resin, and a urethane resin, may contain the resin constituent for toners of this invention within limits which can attain the purpose of this invention. In addition, the above-mentioned vinyl system copolymer may take the structure of cross linkage.

[0031] Moreover, an aliphatic amide and screw aliphatic amide, a metallic soap, paraffin, etc. may be further added by the resin constituent for toners of this invention.

[0032] Although especially the manufacture method of the toner of this invention is not limited, usually, in a resin constituent, further, distributed mixture of the canal nature silica etc. is carried out as the magnetic powder for magnetic toners, and a fluid improvement agent, a release agent, a coloring agent, a charge control agent, and after carrying out heat fusion kneading, it grinds and it is manufactured if needed. In addition, you may distribute the above-mentioned release agent at the time of the polymerization of a resin constituent.

[0033] As the above-mentioned release agent, olefin system waxes, paraffin wax, etc., such as a polypropylene wax and a polyethylene wax, are mentioned, for example. As the above-mentioned coloring agent, carbon black, an aniline black, a copper phthalocyanine blue, quinoline yellow, lamp black, Rhodamine B, a Quinacridone, etc. are mentioned, and 1-10 weight section addition is usually carried out to the resin constituent 100 weight section, for example.

[0034] There are two kinds the object for right electrification and for negative electrification of the above-mentioned charge control agents. As the above-mentioned charge control agent for

positive electrification, a Nigrosine color, an ammonium salt, a pyridinium salt, an azine, etc. are mentioned, and a chromium complex, an iron complex, etc. are mentioned as a charge control agent for negative electrification, for example. 0.1–10 weight section addition of these charge control agents is usually carried out to the resin constituent 100 weight section.

[0035]

[Embodiments of the Invention] Although an example is given to below and this invention is explained to it in more detail, this invention is not limited only to these examples.

[0036] [Manufacture of the resin constituent for full color toners]

(Examples 1 and 2 and examples 1–4 of comparison) By the combination composition which installs a reflux condenser, a distilling column, a water decolorator, a nitrogen gas introduction pipe, a thermometer, and stirring equipment in a 2l. 4 mouth flask according to a conventional method, and is shown in Table 2 Dicarboxylic acids [phthalic anhydride (PAn)], diols [1 and 4-cyclohexane dimethanol (CHDM) or ethylene glycol (EG)], and an esterification condensation catalyst [dibutyltin oxide (DBTO)] are taught. at 200 degrees C The esterification reaction was carried out making the water to generate distill from a distilling column. When water stopped having distilled from the distilling column, the esterification reaction was terminated, and the polyester block A was acquired.

[0037] After acquiring the polyester block B similarly by the combination composition shown in Table 2 with another 2l. 4 mouth flask, The polyester block A acquired previously is added, melting mixture is carried out, while removing a distilling column, a vacuum pump is attached, and the inside of a system is decompressed to 5 or less mmHg. by 220 degrees C and stirring rotational frequency 120rpm The isolation diol produced in the condensation reaction was made to distill out of a system, and polyester block-copolymer ** shown in Table 2 – ** were obtained.

[0038] (Example 5 of comparison) Condensation polymerization of carboxylic acids, diols, and the esterification condensation catalyst was carried out in the same reaction procedure as an example 1 by the combination composition shown in Table 2, and polyester random-copolymer ** was obtained.

[0039] [Manufacture of a full color toner]

(Examples 1 and 2 and examples 1–5 of comparison) After mixing the following compound containing these using the resin constituent for full color toners which consists of polyester block-copolymer **-* and polyester random-copolymer ** which were obtained and carrying out melting kneading at 150 degrees C, the jet mill ground in particle size of about 10 micrometers, addition mixture of the 0.3 % of the weight (the product made from Japanese Aerosil, tradename "R972") of the hydrophobic silicas was carried out at this, and the toner was obtained respectively. In addition, resin constituent for full color toners ** - ** are assigned to the numerical order in order of examples 1 and 2 and the examples 1–5 of comparison.

[0040]

– Resin constituent for full color toners (**-**) The 100 weight sections and electric charge control agent (the Hodogaya chemistry company make, tradename "TP-302") 3 weight sections – carbon black (the Mitsubishi Chemical make, tradename "MA-100") The 6.0 weight sections – polypropylene wax (3 ** Chemicals company make and tradename "screw call 660P")

The 4.0 weight sections [0041] Furthermore, it changed to the above-mentioned carbon black, and the Diarylide Yellow was used for yellow, each of a copper phthalocyanine was used for the Magenta at carmine 6B and cyanogen, and the full color toner was produced like the above.

[0042] In order to evaluate the performance of the full color toner using the resin constituent for full color toners and these which were obtained in the above-mentioned examples 1 and 2 and the examples 1–5 of comparison, according to the following method, it measured about the following item, and the obtained result was shown in Table 2 and 3, respectively.

[0043] (1) Fixing nature (fixing temperature)

The iron powder carrier 94.0 weight section with a particle size of about 50–80 micrometers was mixed for the obtained toner 6.0 weight section, the developer was made, this developer was used for the electrophotography copying machine, and the duplication of two or more sheets was created from the non-established picture. On the occasion of the copy, the setting temperature

of the heat fixing roll of an electrophotography copying machine was raised per 1 degree C, and the minimum fixing temperature was measured. With the above-mentioned minimum fixing temperature, the fixing picture was ****(ed) according to the conventional method with the sand rubber for typewriters, and setting temperature was raised one by one, it went, and the fixing picture made fixing temperature setting temperature in case the concentration will not change substantially.

[0044] In addition, what converted Fuji Xerox "Acolor686" into the examination was used for the electrophotography copying machine.

[0045] (2) Setting temperature of the heat fixing roll of an offset-proof nature electrophotography copying machine was made into 190 degrees C, it copied continuously from the non-established picture using the same developer as what was used for the preceding clause, the existence of generating of the offset at the time of toner fixing was observed by viewing, and what generating of "O" and offset was accepted in in what generating was not accepted in was evaluated as "x."

[0046] (3) Fixing surface smooth nature (gloss)

The same continuation copy (setting temperature of a heat fixing roll : 190 degrees C) as the offset-proof sex test of the preceding clause was performed, about the sample of the stable stage without generating of offset, the gloss was measured and fixing surface smooth nature was evaluated. Evaluation made "*" "O" and less than 50 or more 45 gross, and made less than 45 gross "x" for 50 or more grosses. In addition, measurement of gloss used the U.S. Gardner glossmeter (a "gross guard", 60 incident angles).

[0047] (4) Quality of image (existence of fogging)

It copied continuously from the non-established picture using the same developer even as the preceding clause at the fixing temperature obtained by the fixing nature of the 1st term, and the existence of fogging of the fixing picture of the 100th sheet was observed by viewing from the copy start, and what generating of "O" and fogging was accepted in in what fogging was not accepted in was estimated as "x."

[0048] (5) A shelf-life profit **** toner **** 20g, and enclose with every 200ml reagent bottle. After saving in a 50-degree C thermostat for 48 hours, the Hosokawa Micron CORP. make and a "powder circuit tester PT-E type" are used, the condition for the amplitude of 1mm, and 10 seconds The screening test was performed and that to which it exceeded "O" and 1g for that whose amount of survival of the plus sieve of 250 micrometers of openings was 1g or less was estimated as "x."

[0049] (6) what sampled the sample at random than what was continuously copied from the non-established picture using the same developer even as the preceding clause at the fixing temperature obtained by the fixing nature of the 1st term of transparency, observed the tint of the halftone portion after fixing visually, and was able to reproduce the halftone — "O" — although it was reproducible, estimated a little dissatisfied thing as "**", and what was not able to be reproduced estimated as "x"

[0050]

[Table 2]

		配合組成 (モル%)				物性		
		ジメチルシロキサン酸	シリカ		触媒	重量平均 分子量 M_w ($\times 10^{-3}$)	ガラス転移点 ($^{\circ}\text{C}$)	ガラス転移点 ($^{\circ}\text{C}$)
		PAa	CHDM	EG	DBTO			
ブレンDED共重合体① ブレンDED A/ブレンDED B =70/30	ブレンDED A	70	84	—	0.063	0.85	106.3	62.1
	ブレンDED B	30	—	36	0.027			
ブレンDED共重合体② ブレンDED A/ブレンDED B =50/50	ブレンDED A	50	60	—	0.045	1.28	107.8	59.0
	ブレンDED B	50	—	60	0.045			
ブレンDED共重合体③ ブレンDED A/ブレンDED B =95/5	ブレンDED A	95	114	—	0.085	0.89	124.2	76.1
	ブレンDED B	5	—	6	0.005			
ブレンDED共重合体④ ブレンDED A/ブレンDED B =30/70	ブレンDED A	30	36	—	0.027	2.80	117.2	55.9
	ブレンDED B	70	—	84	0.063			
ブレンDED共重合体⑤ ブレンDED A/ブレンDED B =50/50	ブレンDED A	50	60	—	0.045	3.50	137.4	75.2
	ブレンDED B	50	—	60	0.045			
ブレンDED共重合体⑥ ブレンDED A/ブレンDED B =60/50	ブレンDED A	50	60	—	0.045	0.28	91.5	45.0
	ブレンDED B	50	—	60	0.045			
ブレンDED共重合体⑦		100	60	60	0.090	2.60	120.1	62.4

[0051]

[Table 3]

	樹脂組成物	定着性 (定着温度 ℃)	耐オフセット性	定着表面平 滑性(光沢)	画質 (ドット)	保存性	透明性
実施例	1 プリマ共重合体①	125	○	○	○	○	○
	2 プリマ共重合体②	127	○	○	○	○	○
比較例	1 プリマ共重合体③	143	○	×	○	○	×
	2 プリマ共重合体④	134	○	○	○	○	○
	3 プリマ共重合体⑤	153	○	×	○	○	×
	4 プリマ共重合体⑥	112	×	○	×	×	○
	5 リンゲル共重合体⑦	139	○	○	○	○	○

[0052] although the toner of examples 1 and 2 shows good fixing nature also at low temperature, it excels also in offset-proof nature and shelf life, and fogging is not generated, either, but it excels also in the transparency it is opaque to the factor of the repeatability of a halftone, and the balance of many of these performances is only held good, so that more clearly than Table 3 — **** — it does not stop but it turns out that it is quality On the other hand, there were fogging and generating, good quality of image is not obtained, and reappearance of a halftone did not have [the toner of the examples 1 and 3 of comparison] not much well fixing nature not much good [offset-proof nature and shelf life were bad, and] although the toner of the example 4 of comparison showed good fixing nature at low temperature, either. Although the toner of the example 2 of comparison had high fixing temperature a little, the toner of the example 5 of comparison using the polyester resin which consists of the conventional random copolymer barely as binding material was *****.

[0053] [Manufacture of the resin constituent for monochrome toners]

(Examples 3 and 4 and examples 6-10 of comparison)

By the combination composition shown in Table 4 using the same condensation polymerization equipment as what was used for manufacture of a polyester block copolymer The dicarboxylic-acid [terephthalic-acid [(TFA)] diols [ethylene glycol shown in Table 4 (EG), diethylene glycol (DEG) Triethylene glycol (TEG) 1, 3-propylene glycol (PG), neopentyl glycol (NPG)], a trivalent carboxylic acid [1, 2, and 4-benzene tricarboxylic-acid (anhydrous): (TMA)], and an esterification condensation catalyst (it is the same as an example 1) are taught. Bridge formation polyester resin was prepared like the polyester block copolymer. The flow softening temperature and the glass transition point of bridge formation polyester resin which were obtained were collectively shown in Table 4.

[0054]

[Table 4]

	配合組成 (モル%)					物性		
	ジメチルベンジジン酸	ジメチル		3価のカルボン酸	触媒	フッ素軟化点 (°C)	ガラス転移点 (°C)	
架橋型ポリエステル	TPA 100	PG 82	TBG 18	TMA 14	DBTO 0.01	143.2	62.5	
架橋型ポリエステル	TPA 100	NPG 75	DEG 25	TMA 25	DBTO 0.01	136.5	60.1	
架橋型ポリエステル	TPA 100	EG 40	PG 50	TBG 10	TMA 14	DBTO 0.01	128.4	58.2

[0055] Polyester block-copolymer **-* and polyester random-copolymer ** which were obtained previously were taught to the obtained bridge formation polyester resin according to the combination composition shown in Table 5, after the concentration of this resin constituent poured in toluene so that it might become 40 % of the weight, and it carried out melting mixture under heating stirring further, desolventization was carried out with reduced pressure by the ordinary pressure for 1 hour for 2 hours, and the resin constituent for monochrome toners was obtained.

[0056] [Manufacture of a monochrome toner]

(Examples 3 and 4 and examples 6-10 of comparison) After mixing the following compound containing this using the obtained resin constituent for monochrome toners and carrying out melting kneading at 150 degrees C, the jet mill ground in particle size of about 10 micrometers, addition mixture of the 0.3 % of the weight (the product made from Japanese Aerosil, tradename "R972") of the hydrophobic silicas was carried out at this, and the toner was obtained respectively.

[0057]

- Resin constituent for monochrome toners The 100 weight sections and chromium auriferous color (Orient chemical-industry company make, tradename "BONTORON S-34")

The 1.5 weight section - carbon black (the Mitsubishi Chemical make, tradename "MA-100") The 6.5 weight sections and polypropylene wax (3 ** Chemicals company make and tradename "screw call 660P")

The 4.0 weight sections [0058] In order to evaluate the performance of the monochrome toner using the resin constituent for monochrome toners and these which were obtained in the above-mentioned examples 3 and 4 and the examples 6-10 of comparison, according to the following method, it measured about the following item, and the obtained result was shown in Table 5 and 6, respectively.

[0059] (1) Fixing nature (fixing temperature)

The minimum fixing temperature was measured like the full color toner except having mixed the iron powder carrier 93.5 weight section with a particle size of about 50-80 micrometers for the obtained toner 6.5 weight section, and having made the developer, and having used what converted "7050" by Konica Corp. into the examination as an electrophotography copying machine used for the examination. As the judgment method of the minimum fixing temperature, it changed to the sand rubber for typewriters, and ****(ed) as **** material, using the cotton pad, and setting temperature from which the fixing intensity obtained by the lower formula (1) serves as a value beyond 85% or this was made into fixing temperature. In addition, the Macbeth reflection density meter "RD-914" was used for the picture concentration in a formula (1).

[0060] (2) The skin temperature of the heat fixing roll of an offset-proof nature electrophotography copying machine was gradually changed to the both sides of the elevated-temperature section and the low-temperature section, the toner image of the transfer paper which has the above-mentioned non-established picture was established, and the duplication was obtained. At the time of the above-mentioned imprint, the critical temperature of the elevated-temperature section which has generating of the dirt by the toner in the margin portion of tracing paper, and the low-temperature section was measured, the temperature field without generating of the above-mentioned dirt was made into the non-offsetting temperature field, and width of face of this temperature field was made into non-offsetting temperature width of face.

[0061] (3) The screening test was performed by the same method as a shelf-life full color toner, and the same criteria estimated.

[0062] (4) Quality of image (existence of fogging)

It observed by the same method as a full color toner, and the same criteria estimated.

[0063]

[Table 5]

	配合組成 (重量部)		物性	
	ア [*] ロジック共重合体	架橋ア [*] ロジック	フー軟化点 (°C)	ガラス転移点 (°C)
実施例 3	ア [*] ロジック共重合体① 70	架橋ア [*] ロジック 30	120.7	62.2
実施例 4	ア [*] ロジック共重合体② 60	架橋ア [*] ロジック 40	122.1	59.4
比較例 6	ア [*] ロジック共重合体③ 70	架橋ア [*] ロジック 30	131.6	71.4
比較例 7	ア [*] ロジック共重合体④ 60	架橋ア [*] ロジック 40	126.8	57.5
比較例 8	ア [*] ロジック共重合体⑤ 60	架橋ア [*] ロジック 40	132.9	67.3
比較例 9	ア [*] ロジック共重合体⑥ 70	架橋ア [*] ロジック 30	111.7	49.1
比較例 10	ア [*] ロジック共重合体⑦ 70	架橋ア [*] ロジック 30	129.1	62.4

[0064]

[Table 6]

		非ワザト温 度領域 (°C)	非ワザ ト温度 幅(°C)	定着性 (定着温度 (°C))	保存性	画 質 (25°)
実 施 例 比 較 例	3	100 ↓ ~ 230 ↑	130 ↑	131	○	○
	4	100 ↓ ~ 230 ↑	130 ↑	133	○	○
	6	106 ~ 230 ↑	124 ↑	144	○	○
	7	100 ↓ ~ 230 ↑	130 ↑	138	○	○
	8	113 ~ 230 ↑	117 ↑	145	○	○
	9	100 ↓ ~ 230 ↑	130 ↑	127	×	×
	10	103 ~ 230 ↑	127 ↑	141	○	○

[0065] The toner of examples 3 and 4 shows good fixing nature, and is excellent also in offset-proof nature and shelf life with low temperature, fogging is not generated, either, but the balance of many of these performances is held good, and it turns out that it is quality so that more clearly than Table 6. On the other hand, each toner of the examples 6-10 of comparison shows high fixing temperature relatively, and although the fixing temperature of the toner of the example 9 of comparison is low, quality of image, such as generating of shelf life and fogging, is bad, and it turns out that it is that with which use cannot be presented.

[0066]

[Effect of the Invention] The resin constituent for toners of this invention forms a tough toner paint film, can plaster tracing paper with it firmly, carries out pulverization by heat or the mechanical friction, and neither the circumference nor tracing paper is polluted, or it does not pollute tracing paper unnecessarily by adhesiveness while making the stain pigment of a colorant etc. bind firmly, since it is constituted as mentioned above.

[0067] since the toner of this invention is constituted as mentioned above, in spite of showing good fixing nature, also at low temperature, it excels also in offset-proof nature and shelf life, and fogging is not generated, either, but the repeatability of a halftone is also good and the balance of many of these performances is only held good — **** — it does not stop but any performance is quality

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the flow chart for physical-properties analysis of the resin constituent for toners of this invention.

[Translation done.]